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Pd(111) Surface Step Dynamics During the Growth of Monolayer Graphene

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Pd(111) Surface Step Dynamics During the Growth of Monolayer Graphene

A thesis submitted in partial satisfaction

of the requirements for the degree Master of Science

in Materials Science and Engineering

by

Nai Tong

2014
In situ low-energy microscopy (LEEM) was employed to investigate Pd(111) surface step dynamics during the growth of monolayer graphene. Monolayer graphene was grown via surface segregation of carbon on the Pd(111). To study the Pd(111) surface step...
dynamics, the LEEM images were acquired prior to monolayer graphene growth. The
sublimation of atomic layers from the palladium surface was observed at ~1200 K before
the formation of monolayer graphene. The sublimation occurred by removal of single
spiral steps on the surface. The rotation frequencies of the single spiral and the step
speeds were measured as a function of temperature. The results are related to the
activation barriers of surface processes. Oxidation of graphene on Pd(111) was also
studied in this thesis.
The thesis of Nai Tong is approved

Ya-Hong Xie

Mark S. Goorsky

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University of California Los Angeles

2014
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Chapter 1: Introduction

1.1 What is Graphene

Graphene is a monolayer of carbon atoms tightly packed into a two-dimensional honeycomb lattice.¹ The thickness of monolayer graphene is 0.335 nm. Fig. 1 shows the structure of monolayer graphene. Because of its two-dimensional structure and unique properties, graphene has been attracting great interest in fields of material science and condensed matter physics.

![Image of graphene structure]

Figure. 1 The structure of graphene (carbon atoms arranged in honeycomb lattice). Reproduced from http://en.wikipedia.org/wiki/Graphene

Graphene can be considered as the basic building unit for zero-dimensional (0D) fullerenes, 1D nanotubes, and 3D graphite. Fig. 2 shows a schematic representation of
these carbon allotropes.\textsuperscript{2} Due to its 2D structure, graphene exhibits unusual electrical, mechanical, optical, and thermal properties.

![Figure 2. Schematics of carbon allotropes. Reproduced from Ref. 2.](image)

In graphene, carbon atoms undergo sp\textsuperscript{2} hybridization.\textsuperscript{3} There are three σ bonds formed per carbon atom, as one 2s orbital is mixed with two 2p orbitals. The remaining 2p orbital forms a π bond for each carbon atom. The carbon-carbon distance is 1.42 Å, as shown in Fig. 3. The lattice constant of graphene is 2.46 Å. As shown in Fig. 3, \( \overrightarrow{a_1} \) and \( \overrightarrow{a_2} \) are the primitive lattice vectors of unit cell of graphene, the length \( \overrightarrow{a_1} = \overrightarrow{a_2} = 2.46 \) Å. Each unit cell of graphene consists of two atoms, A and B, with real space vectors:

\[
\overrightarrow{a_1} = \frac{a}{2} (3, \sqrt{3})
\]
\[ \vec{a}_2 = \frac{a}{2} (3, -\sqrt{3}) \]

Figure 3. Real space lattice of graphene. Reproduced from Ref. 3.

1.2 Properties of Graphene

The electrical properties of free-standing graphene are different from bulk graphite and most materials. Firstly, graphene has higher electron mobility compared to other commonly used electronic materials such as Si and Ge. For example, at room temperature (300 K), the electron mobility \( \mu \) of graphene can be \( \sim 15,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \), whereas the electron mobility of silicon is only \( \sim 1,400 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \). At low temperature, Kim and co-workers measured the electron mobility of free-standing graphene to be \( \sim 200,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \). They have also measured the mobility of graphene supported on hexagonal boron nitride (h-BN), which is found to be \( \sim 140,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \) at room
temperature.\textsuperscript{6} Secondly, the charge carriers in graphene can be seen as electrons having zero rest mass.\textsuperscript{1} These massless Dirac fermions behave more like relativistic particles, described by (2+1) Dirac equation,\textsuperscript{7} which gives rise to unusual phenomena such as an anomalous quantum Hall effect.\textsuperscript{8} In the first Brillouin zone for graphene, there are six intersection points between conduction band and valence band. The intersection point is defined as Dirac point.\textsuperscript{7} The charge carriers have linear dispersion relationship at Dirac point, which is the location of Fermi level, as shown in Fig. 4. It is this topology of the bands that gives rise to all these exotic electronic transport properties. The lack of an energy gap between conduction and valence bands makes graphene to be a semiconductor with zero band gap.

Figure 4. Graphene band structure. Reproduced from Ref. 2.
Graphene is one of known materials with the highest mechanical strength and stiffness. The elastic properties and intrinsic breaking strength of free-standing monolayer graphene membranes were measured to be 1 TPa and 42 N m\(^{-1}\) by nanoindentation in an atomic force microscope.\(^9\) Graphene is also structurally malleable, i.e. it is able to sustain reversible elastic deformations in excess of 20%.\(^10\)

Graphene has unique optical properties. Graphene is found to absorb incident white light, although its thickness is only one atom thick. As shown in Fig. 5, optical absorbance of graphene is measured to be 2.3 ± 0.1%, practically independent of wavelength.\(^11\)

Graphene is visible to the naked eye if it is on a proper substrate.

![Figure 5. Optical absorbance of graphene. Reproduced from Ref. 11.](image)
The thermal conductivity of graphene at room temperature is up to 5300 W/mK.\textsuperscript{12}

Graphene has negative thermal expansion coefficient of $-7 \times 10^{-6}$ K$^{-1}$ at room temperature, while in comparison, it is $-1 \times 10^{-6}$ K$^{-1}$ for graphite.\textsuperscript{13}

1.3 \textit{Applications of Graphene}

Due to the unique properties of graphene, it has many promising applications. For example, graphene layers, owing to low atomic number (Z), high degree of crystallinity, and atomic-scale thicknesses, are attractive as supporting membranes in transmission electron microscopy for high-resolution imaging.\textsuperscript{14} A technologically promising application is using graphene as a transparent conductor instead of indium tin oxide (ITO).\textsuperscript{15} ITO is widely used as transparent conductive coatings for liquid crystal displays (LCD), touch panels, and solar cells.\textsuperscript{16,17,18} However, indium is relatively rare and expensive and ITO is brittle. The low-cost graphene with its extraordinary thermal, chemical, and mechanical stabilities, and high transparency is desirable for future optoelectronic devices, for example, as transparent electrodes in solar cell and LCD displays. Graphene can also be used in field emission displays\textsuperscript{19,20,21} and graphene based
field effect transistor, due to its extraordinary electrical properties. Graphene has two surfaces with no bulk between so that can be used to make graphene-based gas sensors which has the ultimate sensitivity, detecting single gas molecules attached to it. Another promising application is to use graphene-based anode instead of graphite in Li-ion battery with higher energy density and durability. For example, electrodes made up by graphene-Si composites exhibit high-storage capacities and good cycling stability.

1.4 Graphene Growth Methods

The first successful method of free-standing graphene synthesis is mechanical exfoliation of graphite. It is well known that graphite is made up of many graphene layers. The individual graphene layers within graphite are bound by weak van der Waals forces. Thus, it is possible to peel graphene layers from high purity graphite. By repeated peeling, monolayer graphene can be extracted. This method is called micromechanical cleavage or Scotch-tape method, shown in Fig. 5. Although this is a simple and cheap way to produce high-quality graphene, it may not be suitable for producing large-area graphene of
uniform thickness and is generally restricted to laboratory experimental research.

Figure 5. The micromechanical cleavage method of producing graphene. Reproduced from Ref. 29.

A popular approach of graphene growth is the conversion of SiC(0001) to graphene by sublimation of silicon atoms at high temperatures.\textsuperscript{30} Because \{0001\} surfaces of SiC are polar, with either Si- or C-terminations, graphene growth kinetics on these faces are different. For example, the thickness of graphene grown on Si-face can be easily controlled by growth temperature, whereas graphene grown on C-face tends to have non-uniform thickness.\textsuperscript{31,32} Graphene growth rate on Si-surface is slower than that on C-face, and is strongly bonded to the substrate.\textsuperscript{33,34} Previous studies have shown that
electron mobility in graphene grown on C-face is higher than that in graphene grown on Si-face.

In addition to the free-standing graphene and epitaxial graphene on SiC, another promising, potentially inexpensive and scalable approach is synthesis of graphene via vapor phase deposition on metal surfaces. It is found that graphene can be grown on transition metal substrates such as Ru, Ir, Ni, Pd, Co, Re, Pt, and Cu. There are two methods for graphene preparation on metal surfaces: (i) surface decomposition of carbon-containing molecules and (ii) segregation of bulk-dissolved carbon on the surface. In the former growth method, graphene can be grown via simple thermal decomposition of hydrocarbons on the surface. The heated sample surface is exposed to hydrocarbons, due to which the hydrocarbon molecules decompose to form carbon and hydrogen. The transition-metal surface acts as a catalyst, enhances the decomposition of the precursor (hydrocarbons), and promotes the deposition of carbon atoms on the transition-metal surface. This surface-catalyzed process can be understood as a process involving a chemical reaction on the active metal surface. And this process is
suppressed after the surface is fully covered with graphene. During the whole process, there are several experimental factors, such as crystal structure, lattice parameter, flux of precursor, growth temperature, and pressure of the system that can determine the morphology and thickness of the graphene films.

Another method to grow graphene involves segregation of carbon upon cooling from a metastable carbon-metal solid solution onto the surface of the metal in the form of graphene. Due to the temperature-dependent differences in carbon solubilities in the metal, carbon atoms can be controllably segregated from the bulk metal to the surface to form graphene layers of desired thickness. Thus, carbon solubility in the metal and the growth conditions define the morphology and thickness of graphene. Li et al. used isotopic labeling of the carbon precursor to study the mechanism and kinetics of graphene growth on Ni substrates. Since the carbon solubility in Ni is as high as ~1.3 wt.% at 1273 K, carbon diffuses into the metal first before segregating and precipitating on the surface to form graphene. The graphene formed on the Ni surface is a uniform mixture of isotopic carbons as confirmed by Raman spectroscopy. The results of Li’s experiment
confirmed the growth of graphene via segregation of carbon on Ni surface.

As part of my thesis, Pd(111) surface step dynamics during graphene growth and oxygen influence on graphene growth are both investigated. Pd is known to form one of the best electrical contact with graphene exhibiting low contact resistance, which is crucial for graphene based electronic applications. The carbon solubility in Pd is 1.4 wt.% at 1023 K. The lattice mismatch between Pd(111) and graphene is 9.8%. Graphene grown on Pd typically has multiple domains and exhibits moire patterns with large periodicities. That is, graphene is rotated with respect to the substrate. A few of the rotation angles observed are -2°, -5°, -10°, +17°, +22°, and +26° with a measurement uncertainty of ±1°. Semiconducting graphene islands with a band gap of 0.3 ± 0.1 eV were found on Pd(111). Graphene has been grown on Pd(111) surface by segregation method. Mok et al. investigated kinetics of monolayer graphene growth on Pd(111) by segregation using low-energy electron microscopy (LEEM). LEEM results showed that the growth rate of individual graphene domains is constant, based upon which the authors concluded that graphene growth is controlled by the rate of C adatom attachment to the domain.
edges. Domains nucleating at later times grew faster than those formed at earlier times, which suggests that the concentration of C adatoms is increasing with increasing time. Due to the combination of strong C-Pd binding energy and the presence of a barrier for attachment of C adatoms to graphene, C adatoms can be as stable as graphene on Pd(111) with extremely large concentration. Given the importance of graphene-Pd contacts, it is important to understand the factors controlling carbon solubility in Pd, graphene-Pd interactions, and the thermal stability of graphene-Pd interfaces.

Understanding the oxidative etching process of graphene is significant for both science and technology. It has been found that oxygen atoms can diffuse between the graphene layer and substrates to accomplish decoupling at a low-temperature oxidation process. Two kinds of oxidation mechanisms were found on Ru(0001), involving directly etching graphene islands by oxygen and etching owing to a net evaporation rate into the adatom gas to restore the equilibrium concentration. Oxidation process can also create defects in graphene. I have investigated the internal stability of bare Pd and the oxygen influence on graphene growth on Pd(111) in this thesis.
Chapter 2: Experimental Characterization

2.1 Basics of LEEM

In my thesis work, ultra-high vacuum low-energy electron microscopy (UHV LEEM) is used for the investigation of the Pd(111) step dynamics during the monolayer graphene growth. The concept of LEEM was proposed and developed by Ernst Bauer over five decades ago. The first LEEM test was conducted in the 1960s, and the reasonable quality LEEM images were obtained in mid-1980s.

LEEM is a surface sensitive technique for observing the dynamics of surfaces with nanometer resolution in vacuum or in the presence of gases. It is a surface imaging technique that relies on interaction between low energy electrons and the specimen surface. A parallel beam of low-energy electrons, ranging from 1-100 eV, is used as the incident beam. Electrons specularly reflected from the sample surface are collected by a detector to form either real space images or reciprocal space diffraction patterns of the surface. A LEEM system consists of an illumination system, a beam separator, an
objective lens system, and an imaging column. Fig. 6 shows a simplified schematic of a LEEM system.

Figure 6. Simplified LEEM schematic. Reproduced from Ref. 59.

In the illumination column, electrons from the electron emitter are formed into a parallel beam by a series of lens. The electron beam is then deflected by a prism optics to impinge orthogonally onto the specimen surface. The electrons are decelerated by an applied bias to a low energy, usually 1 to 100 eV, to interact with the specimen surface. Electrons scattered by the surface are deflected by the same prism but in the opposite direction. The scattered electrons are reaccelerated and collected by an imaging column. The size of the
electron beam incident on the specimen surface is defined by an illumination aperture, which is also used to select the electron diffraction area. There is also a contrast aperture in the imaging column to select the electrons that are collected at the detector. The variations in crystal surface orientation, composition, structure and topography, affect electron reflectivity, and give rise to contrast in the LEEM images. In addition, interference between the electron beam reflecting from surfaces of different heights (e.g., surface terraces vs steps) lead to phase contrast. Thus LEEM images can provide the information regarding surface morphology, structure, film thickness, domain orientation, and composition.

Based on the principle of LEEM imaging, LEEM can offer dynamical observation of surface morphology, structural changes, and simultaneous determination of surface electronic structure. LEEM images directly give the information about the real space structure of the specimen. LEEM can also be used to gather electron diffraction patterns to determine the crystallographic orientation of the specimen. From electron reflectivity measurements by LEEM, surface work function can be calculated. Thus, LEEM is well
suited for study of the graphene synthesis.

For the experimental part of my thesis, all the graphene growth experiments are performed on carbon-saturated bulk Pd(111) single crystals in an UHV-LEEM system. The base pressure of the system is $9.7 \times 10^{-9}$ Torr. Fig. 7 is a schematic of the UHV-LEEM system used for graphene synthesis and characterization. To maintain the UHV condition, four turbomechanical pumps, three ion pumps, and one titanium sublimation pump are used. Samples are cleaned by Ar$^+$ ion sputtering in the preparation chamber and transferred to the main chamber for in situ LEEM characterization.

![Figure 7. UHV-LEEM system schematic used for graphene growth experiment.](image-url)
2.2 Sample Preparation

The Pd(111) single crystal substrates were first saturated with carbon by annealing at 1173 K overnight in an atmosphere of 90% Ar - 10% CH₄ at 760 Torr in a tube furnace. The substrates were then air-transferred into the UHV-LEEM system, degassed, and cleaned in the preparation chamber by repeated cycles of sputtering with 1.5 keV Ar⁺ ions and annealing at 1173 K. The substrates were heated from the backside using an electron beam. A type-C thermocouple spot welded to the sample holder was used to monitor the substrates temperature. After cleaning, the substrates were transferred to the main chamber in UHV atmosphere.

Graphene was grown by the segregation of carbon from the bulk onto the Pd(111) surface. In this process, the Pd(111) substrates were first heated to a high temperature T between 1153 K and 1233 K, and then cooled to a lower temperature. At T > 1153 K, bulk solubility of carbon in Pd is relatively high, ~1.4 wt.%⁴⁹ and all the carbon atoms stay in the bulk. Carbon solubility decreases as the temperature decreases. The excess carbon atoms precipitate out to the surface, which nucleate and grow as graphene. Due to the
relationship between carbon solubility and growth temperature, the amount of carbon segregated to the surface can be determined. By adjusting the growth temperature, the thickness of graphene layers can be precisely controlled. Moreover, by increasing and decreasing the substrate temperature, graphene can be dissolved and regrown at the same region of interest on the surface. This approach has proven to be very useful to observe the dynamics of both the substrate steps and graphene growth. In my experiments, bright field LEEM images were obtained at the rate of 5 frames/s. Incident electron energy $E$ is 2.26 eV. Typical field of view is 20 $\mu$m and pixel resolution in the images is 223 Å/pixel.

As part of my thesis, oxidation of graphene on Pd (111) was also studied. A base pressure of approximately $9.7 \times 10^{-9}$ Torr was maintained for UHV growths. For graphene oxidation, molecular oxygen was introduced with the aid of a leak valve. Time-dependent changes in areas $A(t)$ of graphene domains were determined from the LEEM images with Image J, an image processing software. The batch processing code used for area measurement is presented in appendix I.
Chapter 3: Results and Discussion

3.1 Sublimation of Atomic Layers from a Pd(111) Surface

In order to investigate the thermal stability of the Pd substrate surface prior to the growth of graphene, I measured the surface morphological changes occurring on the surface during annealing in UHV at high temperatures. In a typical experiment, the Pd(111) sample saturated with carbon was first heated to the temperature $T$ that is sufficiently high to retain all the carbon in the bulk. In my experiments, Pd(111) surface is found to be free of carbon at $T = 1245$ K. It is found that monolayer graphene nucleates and begins to grow at a lower temperature $T \sim 1160$ K. Since Pd vapor pressure is $\sim 7.5 \times 10^{-8}$ Torr at these temperatures, Pd atoms sublime from surface. Since sublimation is a thermally-activated process, the rate of Pd atom desorption depends on the substrate temperature. In these Pd:C alloys, since the surface carbon atom composition changes with temperature, the Pd atom desorption kinetics is expected to be different from that of pure Pd surface. In the LEEM images, the Pd(111) surface is seen to erode mainly through winding motion of single-spiral steps that are pinned by bulk dislocations.
terminating at the surface. The appearance of spiral steps is more pronounced in C-containing Pd samples, and maybe related to the presence of carbon in the crystal. This process slows down as the substrate temperature decreases. This is because the desorption is a thermally-activated process. Moreover, as T decreases from 1245 K to 1174 K, surface C adatom concentration is expected to increase. While we do not know the exact amount of C on the surface, we expect that it will influence the Pd desorption kinetics.

Figure 8. Typical LEEM image (field of view = 20 µm, and E = 2.26 eV) of single spiral step on Pd surface (right image is the magnification of region A).

Fig. 8 is a representative LEEM image, with a field of view of 20 µm, obtained at t = 142 s, with the sample temperature T = 1173 K. The time t = 0 s corresponds to the time at which the sample temperature reaches T = 1217K. The base pressure during the experiment is 9.7×10⁻⁹ Torr. Region labeled A shows a spiral step. This type of feature
arises as a result of a bulk dislocation terminating at the surface, and the vertex of the spiral is at the end point of the dislocation core.\textsuperscript{64} In my experiments, most of the spirals appear isolated and away from other spiral step structures.

![LEEM images](image)

Figure 9. LEEM images (E = 2.26 eV) of spiral step on Pd(111) acquired during annealing at T = 1174 K as a function of time t = a) 0 s, b) 20.1 s, c) 40.5 s, and d) 60.8 s.

Figures 9 (a-d) present time-sequence images obtained at T = 1174 K of a single spiral with its vertex corresponding to one of the end points of surface-terminated bulk
dislocation. The time $t = 0$ s corresponds to the time at which the sample temperature reaches $T = 1174$ K. The spiral structures shown in Figs. 9 (a-d) are geometrically identical to each other after one full rotation in $\sim 20$ s, which is the time period of the spiral step rotation. It is found that the winding motion of single spiral is periodic with a constant time period $\tau$ over an extended period of time. $\tau$ varies, however, with the sample temperature. In my experiments, $\tau$ increases from 2.2 s to 25.4 s with decreasing temperature from 1245 K to 1166 K.

Figure 10. LEEM images ($E = 2.26$ eV) of one full spiral step rotation in 20 s at $T = 1174$ K, at a function of time $t =$ a) 103 s, b) 106 s, c) 109 s, d) 112 s, e) 115 s, f) 118 s, g) 121 s, h) 123 s.
Figures 10 (a-h) present time-sequence images obtained at $T = 1174$ K of one full spiral step rotation with a time period of 20 s. The time $t = 0$ corresponds to the time at which the sample temperature reaches $T = 1174$ K. As discussed before, the spiral step arises from the screw dislocation on the Pd surface. Due to the dislocation, the step winds itself in a spiral way that a single screw dislocation sends out successive turns of steps. So the spiral rotates, or winds around its vertex, as a function of time. A new atomic step arises from every full rotation.

Figures 11 (a-d) present snapshots of the single spiral step at different temperatures. The spiral step structure remains the same at different temperatures.
Figure 11. Temperature dependence of single spiral step a) $T = 1216$ K, b) $T = 1207$ K, c) $T = 1194$ K and d) $T = 1174$ K.
Figure 12. Plot of the angular frequency \( \omega \) of a spiral step on Pd(111) as a function of temperature \( T \).

The rotation frequency \( \omega = \frac{2\pi}{\tau} \) of the single spiral is plotted as a function of temperature \( T \) in Fig. 12. From Langmuir's theory,\(^{65}\) the rate of sublimation can be expressed as

\[
\text{Rate of sublimation} = \text{Rate of evaporation} - \text{Rate of condensation}
\]

\[
\text{Rate of evaporation} = A\sqrt{T}e^{\frac{\lambda}{RT}}/\text{cm}^2/\text{sec}
\]

\[
\text{Rate of condensation} = \alpha p\frac{M}{\sqrt{2\pi RT}}/\text{cm}^2/\text{sec}
\]

where \( A \) is a constant, \( T \) is the absolute temperature, \( \lambda \) is a constant, \( R \) is the gas constant, \( M \) is the molecular weight, and \( p \) is the pressure.
constant, $\alpha$ is a constant, $M$ is the molecular weight, and $p$ is the partial pressure of the sublimed substance in the gas phase. Thus, the rate of sublimation is

$$\frac{dm}{dt} = A \sqrt{T} \cdot e^{-\frac{\lambda}{RT}} \cdot \sqrt[2]{\frac{M}{2\pi RT}}$$

In the state of equilibrium,

$$\frac{dm}{dt} = 0$$

Then,

$$A \sqrt{T} \cdot e^{-\frac{\lambda}{RT}} = \alpha p_{\infty} \sqrt[2]{\frac{M}{2\pi RT}}$$

where $p_{\infty}$ is the vapor pressure of the solid.

Thus,

$$\frac{dm}{dt} = \alpha \sqrt[2]{\frac{M}{2\pi RT}} (p_{\infty} - p)$$

The process of sublimation of a crystal surface with steps can be seen as the opposite process of growth of such surface. It can be divided into three steps: i) detachment of adatoms from the step, ii) surface diffusion of adatoms to the interior of the single spiral, and iii) desorption of adatoms into vapor.
We note that, at any given T, the shape of the spiral step geometry and step-step spacing are preserved during this sublimation process indicative of fast diffusion of atoms along the step edges. And, changing the T leads to a change in step-step spacing (see Fig. 11). This is because the step-step spacing is determined by the surface diffusion lengths, which change with T. Such spiral step kinetics have previously been observed\textsuperscript{67} and attributed to the surface sublimation, not the mass transport between the surface and bulk.

With each full rotation of the single spiral, a full atomic layer is removed from the surface due to sublimation. Thus, the rotation frequency $\omega$ of the single spiral is proportional to the sublimation rate, which is proportional to $\exp[-(E_f + E_a)/k_T]$, where $E_f$ is the barrier for adatom detachment from the step edge and $E_a$ is the adatom desorption barrier.

From an Arrhenius plot of the data in Fig. 12, I determine that the overall barrier $E_f + E_a = 3.8 \pm 0.1$ eV. This value is comparable to the enthalpy of sublimation of Pd, 3.9 eV.\textsuperscript{68} The enthalpy of sublimation is obtained by adding the enthalpies of fusion and vaporization. Our measured activation energy is not the same as the barrier for vacancy island nucleation, which is likely higher. Although the range of temperatures and spiral
statistics are limited, it appears that the surface desorption of Pd, despite the T-dependent
change in C adatom concentration appears to be thermally-activated with a unique
activation barrier. Additional experiments are necessary to confirm this behavior.
3.2 Oxidation of Graphene on Pd(111)

Figure 13. Top panel: LEEM images of bare Pd island (dark) during graphene (gray) dissolution at 1192 K after 0, 326, 545 and 980 s (from left to right) of exposure to oxygen. middle panel: time-dependent change of area in Pd island. Bottom panel: oxygen pressure as a function of time.

LEEM was used to monitor the size of bare Pd islands during graphene dissolution both
in UHV and in presence of oxygen at temperature $T = 1192 \text{ K}$. Graphene dissolution is
the opposite process of graphene growth. Fig. 13 summarizes results of a typical experiment. The top panel in Fig. 13 shows LEEM images of the bare Pd islands (darker contrast) growth during graphene (gray contrast) dissolution. In these images, the contrast of island remain constant. The time $t = 0 \text{ s}$ corresponds to the time at which the sample temperature reaches $T = 1192 \text{ K}$ with pressure $p = 3.4 \times 10^{-9} \text{ Torr}$. The bottom panel shows the changes in oxygen partial pressure as a function of time during the whole experiment. In this experiment, $O_2$ was introduced during graphene dissolution, increasing from $p = 3.4 \times 10^{-9} \text{ Torr}$ at $t = 125 \text{ s}$ to $p = 4.8 \times 10^{-6} \text{ Torr}$ and kept unchanged until $t = 495 \text{ s}$ and then stopped. As shown in the middle panel in Fig. 13, the change in Pd island area is plotted as a function of time at different $O_2$ pressures. It was found that the change of Pd island area grew linearly with time $t$. It means that the change in the area $A$ of graphene domain decreases linearly with time $t$, i.e. the areal decrease rate $\frac{dA}{dt}$ of graphene is constant. It is observed that the growth rate of Pd island area increases with increasing $O_2$ pressure from $\sim 0.000064 \mu m^2/s$ to $\sim 0.00123 \mu m^2/s$. After stopping
oxygen at $t = 495 \, \text{s}$, $p = 4.8 \times 10^{-6}$ Torr decreased to $p = 3.6 \times 10^{-8}$ Torr resulted in an decrease of growth rate from $\sim 0.00123 \, \mu\text{m}^2/\text{s}$ to $\sim 0.000106 \, \mu\text{m}^2/\text{s}$. The observed increase in growth rate of Pd island with increasing oxygen pressure can be attributed to direct etching of graphene layers. Under this condition, the etching occurs primarily at or near graphene layer edges. Similar graphene oxidation process has been observed for graphene on Ir(111) and Ru(0001) systems.\textsuperscript{54} Our initial set of experiments suggest that the effect of oxygen on graphene-covered Pd surface is different from the observed on Ru. Additional experiments are need to fully understand the mechanism governing oxidation of graphene on Pd(111).
As part of my thesis work, graphene was grown via segregation of carbon dissolved in the Pd(111) single crystal. The Pd(111) surface steps dynamics was observed by LEEM. Monolayer graphene nucleates at the temperature $T = 1160$ K. Before graphene growth, the Pd surface begins to sublime at $\sim 1245$ K via winding motion of spiral steps. The individual spiral steps rotate at detectable rates. Step movement slows as the sample temperature decreases from $1245$ K to $1166$ K. It is found that the winding motion of single spiral is periodic with a constant time period $\tau$ over an extended period of time. $\tau$ varies from 2.2 to 25.4 s with decreasing the sample temperature. The contrast of single spiral steps decreases at the sample temperature $T = 1166$ K and disappears when monolayer graphene covers the surface. It is due to increasing carbon density on the surface. The overall barrier of Pd rotation is determined to be $E_f + E_a = 3.8 \pm 0.1$ eV, which agrees with the enthalpy of sublimation of Pd. Thus, the single spiral rotation is attributed to the sublimation of Pd.

The oxidation of graphene on Pd(111) was also investigated. The increase in growth rate
of Pd island during graphene dissolution is due to the direct etching of graphene layers.

For the oxidation process during graphene growth, more experiments are needed to understand the oxidation mechanism.
APPENDIX I

IMAGE J SCRIPT FOR AREA MEASUREMENT

```java
path= "G:\LEEM\";
ex_date="041813";
filename="g";
//Define file directory

for (number=1; number<1166; number++) {
    if (number<10) i="00000"+number;
    else if (number>=10 && number<100) i="0000"+number;
    else if (number>=100 && number<1000) i="000"+number;
    else i="00"+number;
    //Define file name loop
    run("Raw...","open=["+path+ex_date+"\"+ex_date+filename+"\"+ex_date+filename+i+.dat] image=[16-bit Unsigned] width=896 height=896 offset=392 number=1 gap=0 little-endian");
    //Open .dat files

    makeRectangle(294, 226, 262, 300);
    run("Crop");
    setAutoThreshold("Default");
    run("Make Binary");
    run("Find Edges");
    //Draw region of interest. Values here are for reference and may vary

    run("Analyze Particles...", "size=150-Infinity circularity=0.00-1.00 show=Nothing display exclude clear");
```
Area=getResult("Area", 0);
perimeter=getResult("Perim.", 0);
f=File.openAsString(path+ex_date+"\\+ex_date+filename+"\\area_data\\"+ex_date+filename+"_area.txt");
g=File.open(path+ex_date+"\\+ex_date+filename+"\\area_data\\"+ex_date+filename+"_area.txt");
print(g, f);
print(g, number+"+Area+"+perimeter+"n");
saveAs("Measurements", path+ex_date+"\\+ex_date+filename+"\\area_data\area of "+ex_date+filename+i+.xls");
//Measure area in region of interest and save measured data

File.close(g);
close();
References

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